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GEBZE TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

TECHNO-ECONOMIC ANALYSIS OF BIOETHANOL PRODUCTION AS A CO-PRODUCT FROM BIOMASS

ÖZGE DOYRANLI

A THESIS SUBMITTED FOR THE DEGREE OF

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T.C.

GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

BİYOKÜTLEDEN YAN ÜRÜN OLARAK BİYOETHANOL ÜRETİMİNİN TEKNO-EKONOMİK OLARAK İNCELENMESİ

ÖZGE DOYRANLI
YÜKSEK LİSANS TEZİ
KİMYA MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
DR. ÖĞR. ÜYESİ HASAN ŞILDIR

GEBZE
2022

GEBZE TEKNİK ÜNİVERSİTESİ	**YÜKSEK LİSANS JÜRİ ONAY FORMU**

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 30/06/2022 tarih ve 2022/33 sayılı kararıyla oluşturulan jüri tarafından 25/07/2022 tarihinde tez savunma sınavı yapılan Özge Doyranlı'nın tez çalışması Kimya Mühendisliği Anabilim Dalı YÜKSEK LİSANS tezi olarak kabul edilmiştir.

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SUMMARY

Biorenewable polymers are crucial for the plastic manufacturing industry because of their advantages in environmental sustainability and the sustainable production of value-added products. These polymers can be produced from low costly biomass such as plant biomass, food wastes, agricultural wastes, and biowastes. Petroleum-based polymers used in the production of food containers, packaging, plastic bottles, etc. can be substituted by bio-based polymers. FDCA is produced from biomass or carbohydrates and has attracted attention as a green and renewable chemical. Additionally, bioethanol is synthesized from lignocellulosic biomass via fermentation of xylose because bioethanol is a high-demanded product as it can be blended with gasoline and used as a fuel. Lignocellulosic biomass does not create food security concerns compared to other feedstocks used for producing FDCA and bioethanol. This thesis aims to evaluate the economic analysis of the FDCA and bioethanol production processes by using the SuperPro Designer simulation program in which bioethanol is produced as a co-product in addition to the primary production of 2,5- Furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF). To validate the process parameters for an industrial-scale process, it is critical to examine the effects of process parameters using a process simulation tool. To this end, two scenarios are investigated. For scenario 1 the direct fixed capital cost of this project is found 84.588.000$, and the payback time is 5.23 years; for scenario 2, the direct fixed capital cost is found 132.117.000 $ and the payback time is 2.49 years.

Keywords: 2,5- Furandicarboxylic acid (FDCA), bioethanol, 5-hydroxymethylfurfural (HMF), lignocellulosic biomass, SuperPro Designer

ÖZET

Biyo-yenilenebilir polimerler, çevresel sürdürülebilirlik ve katma değerli ürünlerin sürdürülebilir üretimi üzerindeki avantajları nedeniyle plastik imalat endüstrisi için çok önemlidir. Bu polimerler, bitki biyokütlesi, gıda atıkları, tarımsal atıklar ve biyoatıklar gibi düşük maliyetli biyokütleden üretilebilir. Biyo-bazlı polimerler gıda kapları, ambalajlar, plastik şişeler vb. üretiminde kullanılan petrol bazlı polimerlerin yerini alabilir. FDCA poliesterlerlerin üretiminde kullanılabilen yeşil ve yenilenebilir bir kimyasal olarak dikkat çekmiştir. Bunun yanında şekerden fermentasyon yoluyla üretilen biyoetanol, benzinle karıştırılıp yakıt olarak kullanıldığı için yüksek talep görmektedir. Lignoselüloz bioatık yiyecek güvenliğiyle ilgili endişe oluşturmadığı için FDCA ve biyoetanol üretiminde kullanılabilirler. Çalışmanın amacı, 5-hidroksimetilfurfural'dan (HMF) 2,5- Furandikarboksilik asit (FDCA) üretimine ek olarak biyoetanolün yan ürün olarak üretildiği prosesin tekno-ekonomik analizini yapmaktır. Endüstriyel ölçekte bir proses yapabilmek için proses parametrelerini incelemek çok önemlidir. Bu tezde, SuperPro Designer programı kullanılarak iki senaryo ele alındı ve doğrudan sabit sermaye maliyeti senaryo 1 için 84.588.000 $ ve geri ödeme süresi 5.23 yıl olarak bulundu, senaryo 2 için doğrudan sabit sermaye maliyeti 132.117.000 $, geri ödeme süresi 2.49 yıl olarak bulundu.

Anahtar Kelimeler: 2,5- Furandikarboksilik asit (FDCA), biyoethanol, 5-hidroksimetilfurfural (HMF), lignoselülozik biyokütle, SuperPro Designer

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I would like to thank my parents, mother, father, and brother for their bottomless love and support.

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LIST of ABBREVIATIONS and ACRONYMS

Abbreviations and Acronyms		**Explanations**
AFPEDF	:	Poly (ethylene dodecanedioate-2,5-furandicarboxylate)
DFF	:	2,5-diformylfuran
FA	:	Formic acid
FDCA	:	2,5-furandicarboxylic acid
FFCA	:	5-formylfuran-2-carboxylic acid
GVL	:	γ-valerolactone
HMF	:	5-hydroxymethylfurfural
LA	:	Levulinic acid
MSP	:	Minimum selling price
PEA	:	Hexanedioic acid
PEF	:	Polyethyelene 2,5-furandicarboxylate
PET	:	Etyhlene terephthalate
TPA	:	Petroleum-derived terephthalic acid

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1. INTRODUCTION

1.1. Motivation

Global warming and environmental concerns have increased the motivation for renewable and sustainable energy sources. The United States Department of Energy reported that 1 billion tons of biomass could be used every year for a sustainable purpose to produce almost 25 billion kg of bioproducts and 228 million m^3 of biofuels (which corresponds to 30% of the annual petroleum-based consumption in the USA) [1]. Lignocellulosic biomass is a promising renewable raw material source that can produce several bio-based products (e.g. chemicals, electricity, and fuels), mostly because of its significant chemical structure consisting of glucose, cellulose, xylose, lignin, extractives, and inorganic components. Forest wastes, sea wastes, plant wastes, leaves, agricultural wastes, and food wastes can be the source of lignocellulosic biomass. The single product approach makes the process unfeasible and disadvantageous because biomass is converted to FDCA and bioethanol. First, cellulose and C_5 sugars must be extracted from lignocellulosic biomass to produce valuable chemicals [2]. Cellulose has the largest proportion (30%-40%) of biomass and has a wide range of applications such as cosmetics, paper, nanotechnology, food, textile, etc. In this process, cellulose is used to synthesize HMF [1]. HMF is categorized as one of the most important organic compounds. HMF can be converted to various types of valuable chemicals for example 2,5-dimethylfuran (DMF), 5-hydroxymethyl-2-furan carboxylic acid, 2,5-diformylfuran (DFF), 5-formylfuran-2-carboxylic acid (FFCA), and FDCA. Among them, FDCA can be used to synthesize polyesters [34].

PET (ethylene terephthalate) is a clear, solid, and lightweight plastic widely used for packaging foods, beverages, and synthetic fibers; manufactured more than 26 million tons annually. For the production of PET, TPA is used as one of the raw materials. PEF (polyethylene furanoate) has recently been taking the place of PET because of better recyclability, gas barrier properties, and thermal properties. In addition to that, PEF can be used for packing applications and 3D printing. However, PEF production required high costly pure FDCA. Therefore, studies of cost-effective FDCA production are crucial to replace eco- friendly FDCA derived- PEF instead of petroleum-derived PET [1].

Bioethanol can be used as an additional fuel material, and bioethanol produced from lignocellulosic wastes reduces CO_2 emissions and fuel consumption. Bioethanol is blended with gasoline with different ratios in different countries. However, the mixing ratio by volume of 10% bioethanol and 90% gasoline does not require engine modifications. This percentage differs in every country. Additionally, bioethanol production can be done using cheap, easy accessibility, and abundant raw materials. Bioethanol has high octane value, less toxicity, and efficient combustion. For that reason, bioethanol accounts for 85% of the total biofuel production in the world. To synthesize bioethanol from lignocellulosic biomass, pretreatment, hydrolysis, and fermentation are required.

1.2. The Objective of the Thesis

This work aims to broadly review and analyze the FDCA production from HMF and bioethanol as byproduct. To this end, a techno-economic evaluation of the FDCA and bioethanol production from lignocellulosic biomass by using a new process was performed using a process simulation tool. SuperPro Designer Simulation tool is used to make the economical analysis of the process for an industrial-scale process. The objectives can be separated into three;

- Separate the carbons inside the biomass and make a cost effective process
- FDCA synthesis can be used as a potential green chemical instead of petrochemicals
- Bioethanol synthesis as a second main revenue which can be blended with gasoline and used as fuel among other application fields

1.3. The Scope of the Thesis

In section 1, the motivation of this thesis will be discussed. In section 2, FDCA, the history of FDCA, synthesis methods of FDCA, application areas of FDCA, lignin treatment, and bioethanol will be discussed. FDCA, bioethanol, and lignin are the revenue sources in this study. In section 3, a technology overview will be discussed. Pretreatment, conversion of cellulose to FDCA, and fermentation will be explained. In section 4, process simulation and economic analysis will be addressed. In section 5, the conclusion and recommendations will be discussed.

2. BACKGROUND

2.1. What is FDCA?

Biorenewable polymers are frequently used in the plastic manufacturing industry, and these polymers positively impact environmental sustainability and decrease global resource consumption. These polymers can be produced by bio-wastes, food wastes, and agricultural wastes called lignocellulosic biomass [5].

PET is commonly used for clothing, packaging, and bottle production fibers. Global production of PET is more than 26 million tons/ year. Petroleum-based terephthalic acid (TPA) has been used for the production of PET via copolymerization with ethylene glycol. PEF poly (ethylene 2,5-furandicarboxylate) is the twin of the PET in chemical structure. PEF gained attention after the US Department of Energy announced its building block FDCA as a potential replacement for purified terephthalic acid (PTA) [1].

FDCA belongs to the furan chemical category, green technology for synthesizing polyethylene furanoate and replacing existing petroleum-based terephthalic acid. It can be easily converted into value-added chemical products such as ingredients, and valuable polymers. Due to its broad spectrum of industrial applications and future market potential, FDCA is categorized as an economically applicable chemical by the US Department of Energy (DOE) [5]. FDCA is noted as hope for synthesizing green polymers such as PEF, which is a sufficient alternative to TPA. PEF is not only a replacement for TPA, but it also has better gas barrier performance, mechanical properties, and recyclability. [9],[11].

Avantium and BASF successfully manufactured FDCA with an MSP of $1000/ton together in a common project. At the beginning of 2020, Avantium located a pilot production plant in the Netherlands to produce 5 kilotons of FDCA by using the ‘YXY’ technology [35]. This technology includes the dehydration of carbohydrates and oxidation to FDCA followed by the polymerization of FDCA to form PEF. Many other companies, including Archer Daniels Midland Company, AVA Biochem, VTT, and Dupont, have developed their Technologies for FDCA production. Petrobras has performed a two step process to convert sucrose, glucose and fructose into HMF and then oxidation to FDCA [33].

Researchers know about PEF for years, and several diverse recipes have been studied by changing the parameters like temperature, pressure, catalyst, stoichiometry, etc. However, there is no scientific publication, starting from transesterification, polycondensation, and solid-state polymerization reports, which affect the molecular weight, melting point, and color [6].

2.1.2. Synthesis of FDCA

The synthesis of FDCA methods is divided into three groups.

- Catalytic conversions of various furan derivatives
- Dehydration of hexose derivatives
- Biological conversion of HMF

2.1.2.1. Chemical Oxidative Production of 2,5-FDCA from HMF

HMF, an organic compound, is produced from cellulose and used as a very important raw material for the synthesis of FDCA. Different systems have been used for the oxidation of HMF, such as with oxygen, Pt supported catalysts, Pd supported catalysts, Au supported catalysts, Ru supported catalysts, Rh supported catalysts, and other oxidizing agents like (H_2O_2, $KMnO_4$, GVL: H_2O,etc.). The steps for the production of FDCA via oxidative production of HMF: 1) hydrolysis of biomass into its components 2) separation of cellulose from lignin 3) dehydration of cellulose to HMF 4) oxidation of HMF to FDCA 5) FDCA purification. In this process, cellulose and lignin are usually separated after pre-treatment because lignin can not be used for the production of FDCA [8].

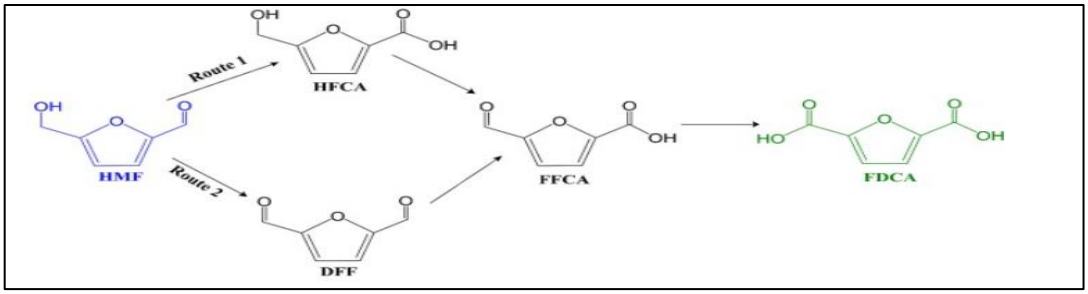


Fig 2.1: Reaction mechanism for HMF oxidation to FDCA.

Oxidation of HMF is studied in the GVL: H_2O (80:20) solvent by 5% Pt/C catalyst under 40 bar pressure for 20 hours with 97% conversion of HMF and 95% yield of FDCA (Table 1, row 1). For economical analysis, it is an obligation that oxidation will be carried out with high HMF concentrations. On the other hand, FDCA has low solubility in mostly used solvents such as water and GVL, but this solubility reaches the peak value at GVL: H_2O (80:20). This peak value is related to the enthalpy of mixing GVL and water. When HMF oxidation is performed with GVL: H_2O (80:20), 5% Pt/C catalyst, and with high HMF concentration, this experiment is resulted in lower FDCA yield because of low water concentration, which was the oxygen source in HMF oxidation (Table 1, row 2). The second experiment is performed while keeping high FDCA solubility with GVL: H_2O (50:50) at 383K over the 5% Pt/C catalyst yielded 94% FDCA. (Table 1, row 3) [4]. In this study, HMF is oxidized to FDCA over Pt supported catalysts via oxidation using GVL: H_2O (50:50 mass ratio) at 383K and 40atm 94% yield), and economical evaluation is done.

Table 2.1: General reaction scheme for FDCA production.

	HMF concentration	Solvent (GVL:H_2O)	HMF:Pt	Time (hours)	HMF conversion (%)	FDCA yield (%)
1	0.5 wt %	80:20	15:1	20	97	95
2	5 wt %	80:20	20:1	20	100	11
3	7.5 wt %	50:50	30:1	20	100	94

2.1.2.2. Dehydration of hexose derivatives

FDCA is produced by two chemists in mucic (galactaric) acid (48:52) v/v in aqueous solution of hydrobromic acid, and this synthesis method is changed many times to obtain high purity and high yield of FDCA. All these reactions required tough conditions like high cost, temperature over 120 °C, and time of the reaction over 20 h. Moreover, all these methods were not efficient (side-products occurred) and yielded less than 50% [10]. Dehydration of the aldaric acids using solid acid catalysts produces furancarboxylates in high yields. This production method avoids the use of unstable HMF as the intermediate in FDCA production.

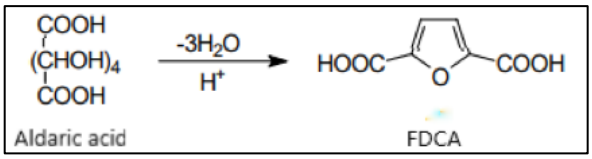


Fig 2.2: Dehydration of aldaric acids to produce FDCA.

Only one reaction gave the promising efficient production of FDCA for future work. On the other hand, despite the mentioned difficulties, methods from this group were considered as easy enough in a work-up and have been operated as laboratory preparative methods [11].

2.1.2.3. Biological conversion of HMF to FDCA

Biological conversion is more convenient because it takes place under mild conditions. During biocatalytic processes, there is a tendency for non-toxic intermediates and by-product formation. Therefore, the production of FDCA from HMF is inspiring but difficult for researchers because biocatalytic routes for FDCA production are not established yet [10].

A fermentative production process of HMF to FDCA with Pseudomonas putida S12 biocatalyst has been investigated using glycerol as a carbon source, and 97% FDCA yield with 99.4 solid recoveries is observed. An increase in temperature increases the biotransformation rate, but the optimal temperature is 28 °C. Increasing the HMF concentration can increase the FDCA yield, but impurity also increases at high concentrations. High concentrations (>2000 mg L−1) reduce cell density due to increased HMF toxicity, while low concentrations (>1500 mg L−1) can support minimal cell growth. These biocatalysts are very sensitive to the feed concentration and pH of the medium, which makes process control more difficult [10].

2.1.3. Application Areas of FDCA

FDCA is utilized for the production of a variety of biochemicals such as succinic acid, macrocyclic ligands, fungicides, thiolene films, poly(ethylene dodecanedioate-2,5-furandicarboxylate) (PEDF), 2-(1-oxopropoxy), hexanedioic acid (PEA), diheptyl furan-2,5-dicarboxylate, isodecyl furan-2,5 dicarboxylate, isononyl furan-2,5-dicarboxylate.

FDCA is used as a crosslinking agent for polyvinyl alcohols, corrosion inhibitor, and pharmaceutical intermediate. FDCA also has potential applications in medicine. The diethyl ester of FDCA has a narcotic effect similar to cocaine. Dicalcium 2,5-furandicarboxylate inhibits the growth of Bacillus megatorium. 75 FDCA-derived anilides perform anti-bacterial features and FDCA itself is a strong complexing agent; together with ions ($Ca^{2+,}$ $Cu^{2+,}$ and Pb^{2+}) has increased its utilization in medicine for the removal of kidney stones. Interestingly, HMF is metabolized via FDCA in mammals, including humans. Manufacturing artificial veins for transplantation via a dilute solution of FDCA in tetrahydrofuran, and many other medical utilizations are under investigation.

2.2. Lignin Treatment

Lignocellulosic biomass consists of a mixture of cellulose, hemicellulose, lignin, and xylan. The cellulose and hemicellulose can be hydrolyzed into sugars and fermented to ethanol. However, lignin is present in all lignocellulosic biomass, but it is not soluble in enzymes, its conversion into ethanol is not possible because of its structural heterogeneity, and it has to be separated from the process to be sold as a separate product. Lignin has advantageous chemical properties such as binding, complexing, dispersing, emulsion-stabilizing. Therefore, it can be used in many fields [9]. Some products that can be synthesized from lignin are listed below:

- Biocomposites
- Filler for materials
- Resins, aerogels
- Thermosetting polymers
- Chemicals
- Carbon fiber / activated carbon

There are several methods to extract lignin from biomass. These methods are kraft processing, sulfite process, application of soda-anthraquinone, acid treatment, organosolv process, ammonia fiber explosion (AFEX), steam explosion, and dioxane-based extraction process. Among them, organosolv method gives the highest purity, but it is a high cost process. Kraft and sulfite processes are cost-effective, but obtained

lignin has impurities. Soda extraction is considered cost effective process with high purity of lignin and less environmental effect. However, their large-scale commercial processes are still under investigation [18]. For any pretreatment, the required energy for the process can not be bigger than the benefit obtained from biomass.

In organosolv delignification process, mostly a mixture of ethanol, acetone, methanol, and water is used in the presence of the low amount of H_2SO_4 at temperatures between 100-250°C. However, using alcohol at high temperatures is related to the generation of high pressures, which means high costly equipment. Therefore, ethanol is frequently used because of its non-toxic, low cost, easy recoverable advantages. Prehydrolysis and organosolv delignification. However, fractionation of wheat straw is studied in the literature in three steps; (i) aqueous pretreatment (ii) organosolv delignification (iii) cellulose hydrolysis. Obtained xylose yield is increased by 4% compared to without pretreatment [7].

2.3. Bioethanol

With the development of technology and due to fact that the damage that fossil fuels are giving to the environment is increasing every year, scientists are searching for new energy sources. The sustainable production of bioethanol and renewable fuel can decrease GHG emissions and petroleum fuel consumption, renewable solid, liquid and gaseous products are formed as a result of biochemical and thermochemical processes of agricultural raw material is called biofuel technology. Biofuels are separated into groups according to sources and types. There are primary (raw) and secondary (refined) biofuels. Ethanol is in the group of refined is chemically same with bioethanol. Ethanol is manufactured from petrochemical sources and bioethanol is manufactured from biological sources. [19]. Bioethanol (ethyl alcohol, $CH_3–CH_2–OH$ or ETOH) is a colorless, volatile and flammable liquid biofuel [14]. Biomass energy is used for both traditional uses (fire for heating and cooking) and modern uses (liquid biofuels, steam and electricity). Ethanol manufactured from biomass has the potential to be sustainable transportation fuel and fuel oxygenate that can replace gasoline [22].

Bioethanol provides so many advantages besides using as a fuel mentioned as following. 1) suitable for transportation and storage: liquid energy (bioethanol) is more advantageous than gas energy (carbon monoxide, hydrogen, hydrogen, methane etc.) because liquid energy does not require liquefaction and it is easy for transportation and

storage. 2) chemical raw material: bioethanol can be used as a raw material for the production of gasoline, butanol or methane because of its unique chemical structure. 3) widely usage in industry: bioethanol is miscible liquid with both hydrophobic, polar, nonpolar, hydrophilic compounds, means makes ethanol most common used solvent in cosmetic, medicine, chemical, food industries [43].

2.3.1. Bioethanol as a Fuel

Bioethanol is produced by using several feedstocks such as grass, wood, corn, sugar beet, sweet sorghum, sugar cane, wood, cereal straw, corn stover, cotton wastes, grasses etc. by fermentation or electrochemical methods [14]. Bioethanol contains 35% oxygen which provides better combustion than gasoline, and it can be used as a fuel when blended with gasoline in different volume ratios. since gasoline demand is so high in the world, bioethanol will reduce this demand as an alternative green fuel [15], [16].

Table 2.2: Comparision between bioethanol and gasoline fuels.

Properties	Ethyl alcohol	Gasoline
Chemical Formula	C_2H_5OH	C_4 to C_{12}
Molecular Weight	46.07	100-105
Carbon content (wt%)	52.2	85-88
Hydrogen content (wt%)	13.1	12-15
Oxygen content (wt%)	34.7	0
Density (g/cm^3)	0.79	0.72-0.75
Octane number	108	90-100
Energy Density (MJ/L)	20,000	32,200
Boiling Point (°C)	16	54-103
Kinematic viscosity @20°C (mm^2 /s)	1,5	0,37-0,44

2.3.2. Globally Bioethanol Production

Bioethanol is the most produced biofuel on earth. 83% of produced biofuel is bioethanol. USA and Brazil are the main manufacturers of ethanol which accounts for about 62% of the world's production of bioethanol. In 1998, world ethanol production 33.3 billion liters. In 1933, corn-alcohol gasoline, which is called ‘gasohol’ is sold by an American oil dealer in Lincoln. Brazil was the biggest manufacturer of ethanol with

16.1 billion liters in 1998.The world [23]. World ethanol production reached a record $62x10^9$ L in 2007, and USA and Brazil accounted for 70% of this record. In 2009, the USA produced $39.5x10^9$ L of ethanol while the second greatest producer Brazil has manufactured $30x10^9$ L of ethanol. From an environmental, economical, and ecological point of view, fossil fuels are not sustainable resources [17]. In 2000, the world bioethanol production was 13.2 billion liters and increased to 109.8 billion liters in 2019 [26]. In 2015, the USA manufactured 58% of the world's overall bioethanol, while Europe and the rest of the world share 14%, and Brazil shares 28% [27]. Global fuel production is shown in (Table 2.3.2.) Fuel production amounts in the USA between 1981-2021 are given in (Figure 2.3.2.) US industry holds for %55 percent of global ethanol production in 2015 [17].

Table 2.3: Bioethanol production amounts in different countries during 2014–2015.

Country	Bioethanol in million gallons
USA	15.000
Brazil	6500
Europe	1369
China	695
India	555
Canada	522
Thailand	310
Argentina	160
Other countries	726

In 2017, the Bangladesh government has allowed using E5 in automobiles sourced from biomass. However, the use of the high amount of raw materials such as 60,000 tonnes of rice or 97,000 tonnes of molasses or 62,000 tonnes of maize to manufacture annual 18 million liters of bioethanol has raised worries about the food security of humans. The main crops of wheat, rice, corn, jute, and sugarcane had 87.19 million metric tonnes of residues has the potential to produce 44.4 million metric tonnes of bioethanol. By using the residues from rice, which is the most hopeful

product in Bangladesh, 31.65 million metric tonnes of bioethanol were produced which is 71% of the overall feedstocks [24].

In Malaysia biomass availability is approximately 47,402 dry kton/year which is from municipal solid wastes, agricultural wastes and forest residues. The domestic demand of bioethanol in Malaysia is 6677 ton/day. Oil palm biomass is selected as a feedstock since Malaysia is the main manufacturer and exporter of palm oil besides paddy and rubber in the world [25]. For this reason, bioethanol would help Malaysia reduce 16.6 million tonnes of carbon dioxide emissions in year 2023 [26].

In Canada, there are various regulations and forbidden the production of bioethanol, such as 5% of the national fuel must be provided by renewable energy sources. This percentage changes in different states: In Ontario renewable energy rate must be 5%, In Saskatchewan it is 7.5%, In Manitoba it is 8.5%. In 2014, 1.74 billion liter of bioethanol is produced in Canada, but it was not sufficient, so rest of it was imported. Corn and wheat are frequently used feedstocks in Canada [30].

In India, bioethanol production is extremely important to reduce the addiction to oil, to make various energy alternatives, for better environmental conditions and to support country's economy. In India, bioethanol production is mostly based on sugars and India is the second largest sugar producing country in the world after Brazil. In 2013, India has manufactured 1.9 billion liter bioethanol while In 2014, 2.1 billion liter of bioethanol is manufactured [30].

China is the world's largest third country in bioethanol production. Yet, food security is top priority in China because of largest population in the world. For this reason, ethanol made from non-food is supported by China and many projects have been developed base on lignocellulosics ethanol production [31]. Corn, wheat and manioc are the feedstocks used in China. In 2018, approximately 87% of ethanol production was made from corn, 11% was made from cassava and sugarcane and the rest 2% was cellulosic feedstock. Currently, China is producing 2.5-3 millions of tons of bioethanol but consumption is 3-3.35 million tons. Therefore about 600.000 tons of fuel ethanol has been imported. There is still a big difference between the consumption and production of fuel ethanol [32].

In Turkey, ethanol-blended gasoline is used for the first time in 1942. TARKİM (Tarımsal Kimya Teknolojileri San. ve Tic. A.Ş.) has the license to produce bioethanol and is the first manufacturer with 30.000.000 liters/year capacity by using corn and wheat as a feedstock. According to TS EN 228 Standards, 5% ethanol can be mixed

with gasoline used in Turkey [29]. According to the existing 12 bioethanol production plants, Turkey is approximately producing 800,000 l/day of bioethanol [27]. Fuel bioethanol production amounts are given in (Table 2.3.2.2.)

Table 2.4 Fuel bioethanol production amounts in Turkey.

Years	Fuel Bioethanol Production in
2011	10.959.891
2012	11.062.518
2013	52.739.172
2014	78.025.859
2015	85.173.494
2016	91.799.547

2.3.3. Feedstocks for Bioethanol Production

The cost of the feedstocks and ease to find the raw materials are significant for sustainable and economical biofuel production. For this reason, bioethanol production is developed every time to overcome the problems of the previous generation feedstocks. 1st generation feedstocks are sugarcane, maize, wheat, paddy, corn, etc. Nevertheless, first generation feedstocks were not sustainable because food has much more priority than the fuel. Additionally, using foods as raw material has increased the food costs. Because of these reasons, different kind of non-edible raw materials are searched like lignocellulosic biomass. 2nd generation feedstocks are sludge, sawdust, crop residues, lignocellulosic biomass, woodchips etc. Compared to other feedstocks used for the production of bioethanol, lignocellulosic biomass does not compete with food crops and they are effective, easily available, and cheaper. Cellulose has high molecular weight and a complex structure requiring high costly enzymatic conversion reaction that has a negative influence on the economy. Because of that, scientists started to search for better cost effective feedstock. 3rd generation feedstocks are macro and microalgae, cyanobacteria etc. Microalgae have high variation and high photosynthetic efficiency, and because of that, they can capture 10-50 times bigger than the plants during photosynthesis and stick the CO_2 into their cells and convert to carbohydrates which are used as a substrate in bioethanol production. These carbohydrates are generally cellulose and starch. But there is no lignin makes microalgae and cyanobacteria much more feasible. Besides, micro-sized raw materials

are easier to handle and vitamins, medicinal drugs, and biopolymers can be produced as a side product besides bioethanol [21].

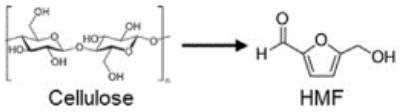
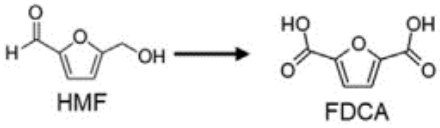
Table 2.5: Bioethanol yields from different energy crops.

Country	Raw material	Bioethanol yield (L/ha)
Brazil	Sugar cane, %100	6641
USA	Corn, 98% Sweet sorghum, 2%	3770 1365
China	Corn, 70% Wheat, 30%	2011 1730
EU-27	Wheat 48% Sugar beet, 29%	1702 5145
Canada	Corn, 70% Wheat, 30%	3460 1075
Serbia	Molasses 50% Cereals (wheat, corn) 50%	260(L/t)[a] 1700-3700

3. TECHNOLOGY OVERVIEW

In this study, the simulated process has the following steps: 1) pretreatment 2) conversion of cellulose to HMF 3) catalytic oxidation of HMF to FDCA 4) fermentation of xylan to bioethanol 5) FDCA purification 6) bioethanol purification. Additionally, recovering and recycling of H_2O, THF, GVL are designed. Chemical reactions and yields are given in (Table 3.1)

Table 3.1: Main reactions and yields.

Reaction	Catalsyst	Reaction	Reaction Conditions	Yield
Cellulose to HMF	H_2SO_4		68.0 atm,210 °C, 45mins	42%
HMF to FDCA	Pt/C		40.0 atm,110°C	94%
Fermantation of pentose to ethanol	Yeast	3Xylose → 4.9 Ethanol + 4.9CO2 + 0.05 Biomass	28°C, 1atm, 72h	84%

3.1. Pretreatment

The purpose of pre-treatment is to break lignocellulose's complex structure and a simple way for microorganisms to access usable sugar in biofuel production. Pre-treatments are separated into groups such as ; mechanical, chemical, physico-chemical and biological. Mechanical pre-treatment includes grinding, pyrolysis, pulsed electric field, shredding, milling, microwave, ultrasound, mechanical extrusion, and downsizing operations. Chemical treatment includes wet oxidation, organosolv, alkaline, ozonation, and concentrated or dilute acid/base usage. Physico-chemical treatment includes ammonia fiber expansion (AFEX), hot water application, oxidative, steam spraying, and CO_2 explosion. Biological treatment includes fungi or some special microorganisms [14], [43].

There are some important points to be taken into consideration for the selection of pretreatment are listed; (i) raw materials and equipments of the selected pretreatment method must have low price, (ii) this method must require less energy, (iii) high efficiency which means a high concentration of sugar to be used in fermentation, (iv) if it is not necessary, do not use chemical pre-treatment and avoid toxic components for environmental impacts, (v) increase the surface area, (vı) low operating and capital costs of the process. However, it is so difficult to find a pretreatment method that meets all requirements mentioned above. However, optimum pretreatment must be selected according to the type of the biomass and the process [3]. In this study, fractionation is used as a pre-treatment method.

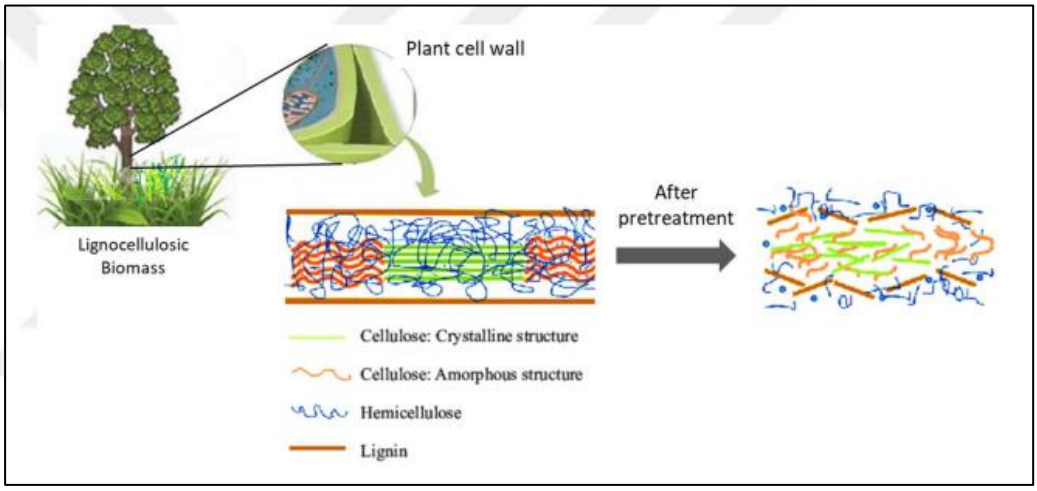


Figure 3.1: Schematic sketch shows pretreatment affect on lignocellulosic biomass.

Lignocellulosic biomass which contains 32.9% cellulose, 15.2 %lignin, 30% water, 17.7% xylan, 4.2%acetate is separated into its components by using 0.1 M H_2SO_4, GVL: H_2O (70:30 mass ratio) for 3 hours, 398°C and 3.4 atm [36]. The purpose of the pretreatment is to increase the reachability to biomass components, the partial or total hydrolysis and solubilization of hemicellulose and the partial hydrolysis, removing the lignin, losing the crystalline structure of cellulose [39]. This pretreatment can be done by using g-valerolactone (GVL) because of its important chemical and physical properties, such as the low vapor pressure of GVL, and the ability to effectively process the component streams downstream within the solvent, which provides a non-enzymatic saccharification method using GVL as a solvent, cost-effective and easily separations, solves typical problems associated with biomass

fractionation, such as continuous biomass feeding, provides high sugar yields at mild temperatures (120 °C), miscible with lignin and sugars in GVL/water mixtures [36],][40].

3.2. Conversion of Cellulose to FDCA

Cellulose is separated from biomass by filter and centrifuge and then converted to HMF at 42% yield by using H_2SO_4 s a catalyst at 68 atm, 210 °C for 45 mins [37]. Cellulose can be converted into glucose at 1% yield, furfural and formaldehyde at 3.2% yield, levoglucosenone at 2.0 % yield, LA and FA at 1.9% yield, levoglucosan at 0.1% yield, and humins at 49.8% yield which will be adsorbed on activated carbon [4]. After HMF production, solvents are recycled by using a distillation column; later on other impurities are adsorbed on activated carbon by using GAC Adsorption. HMF is fed to the stoichiometric reactor to produce FDCA at 93.6% yield at 383 K, 40 atm by oxidation using GVL: H_2O (50:50 mass ratio).

3.3. Fermentation of Xylose to Bioethanol

Any substance that contains sugar inside can be used to manufacture ethanol. Xylose ($C_5H_{10}O_5$) is a preferred sugar because its conversion to furfural, xylitol, and ethanol are common. [41]. Xylose is the most abundant pentose sugar; therefore there are many reports written to search for effective xylose-fermenting microorganisms.

Bacteria, yeast, and fungi are xylose-fermenting microorganisms. *Pichia stipitis* CBS 6054 is one of the yeasts is used for the fermentation of xylose. It gives a high yield, but it is inhibited by co-products that occur in pretreatment. Fungus does not affect during pretreatment however they are not suitable for the commercial industrial process [42]. The most preferred fermenting yeast is *Saccharomyces cerevisiae* because it is categorized as safe; it is able to ferment sugars like mannose, fructose, glucose, and maltose with this yeast it enables to produce of ethanol up to 18% (v/v) concentration [38]. In this study, xylose is converted into ethanol and CO_2 by microorganisms at 28°C, 72h in a batch process.

4. PROCESS SIMULATION and ECONOMIC ANALYSIS

4.1. Facility Simulation and Economical Analysis

SuperPro Designer is a comprehensive and useful tool for engineers and scientists in process development, modeling, manufacturing, evaluation, optimization and process engineering. SuperPro Designer can be used in a wide range of industries such as Consumer Products, Biotechnology, Pharmaceuticals, Food Ingredients and Products, Water Purification, Wastewater Treatment, Bio-Fuels, Metallugry and Material, Waste Valorization, Air Pollution Control. SuperPro Designer can provide cost analysis, optimization, sensitivity and uncertainty analyses, mass-energy balance, and end-of-pipe treatment processes for batch, semi-batch, and continuous processes. Process conditions and parameters such as reaction yield, temperature, reaction conversion rate, yield, residence time, power types, equipment volume, and equipment purchase costs are determined by SuperPro Designer, and these values are used by the software for mass-energy balances and economical evaluation. In addition to that, SuperPro Designer can evaluate labor costs, transportation, laboratory, and waste treatment/disposal costs [29].

The process simulation and the economic analysis of the production of FDCA and bioethanol by using lignocellulosic biomass are executed by using SuperPro Designer in continuous mode for FDCA production, and batch mode for bioethanol production. The processing rate was assumed to be 17ton biomass/h and all equipment costs for the systems (pretreatment, HMF production, FDCA production, FDCA purification lignin separation, bioethanol production) were estimated by using SuperPro Designer.

Project lifetime is taken as 30 years, the startup period is 6 months, the construction period is 36 months, the depreciation period is 7 years, the loan period is 10 years, and the loan interest is 8 years in this project [8]. In this economic analysis, transportation, waste disposal and labor costs are not considered. All the assumptions are references for the cost of items are given in (Table 3.1.)

Table 4.1: Major economic parameters and assumptions.

Items	Costs	References
Tetrahydrofuran price ($/ton)	1532.0	[8]
Oxygen price ($/ton)	40.0	[8]
Sulfuric acid price ($/ton)	110.0	[8]
γ-valerolactone price ($/ton)	1000.0	[8]
Plant life (years)	30.0	[8]
Income tax rate (%)	35.0	[8]
Discount rate (%)	20.0	[8]
Startup time (years)	0.5	[8]
FDCA selling price($/ton)	3885	[12]
Water price($/ton)	0.1	[12]
Biothanol selling price($/L)	1.78	[13]

4.1.1. Direct Fixed Capital Cost

Costs required to build and run a facility are direct fixed capital, indirect costs, equipment costs and contingency costs. Every item in the capital investment cost is calculated by multiplying equipment purchase cost with various proper coefficients. Equipment purchase cost is calculated by using SuperPro Designer databank. Coefficients are given below in the (Table 4.2.) According to that, total plant cost which includes equipment purchase cost, piping, insulation, electrical facilities, is calculated as 42.4 million $ (Table 4.4). Additionally, total plant indirect cost which includes engineering and construction is calculated 25.4 million $. With summing up the cost of contractor's fee and contingency, the direct fixed capital cost is found as 78.0 million $.

Table 4.2 : Coefficients taken from Superpro Designer databank to calculate total plant direct cost.

Capital Investment	Coefficient
Equipment purchase cost	SuperPro Designer databank
Piping (A)	(Equipment purchase cost)*0.2
Instrumentation (B)	(Equipment purchase cost)*0.4
Insulation (C)	(Equipment purchase cost)*0.03
Electrical facilities (D)	(Equipment purchase cost)*0.1
Buildings (E)	(Equipment purchase cost)*1.2
Yard Improvement (F)	(Equipment purchase cost)*0.15
Auxiliary Facilities (G)	(Equipment purchase cost)*0.4
Engineering (H)	(Direct cost)*0.55
Construction (I)	(Direct cost)*0.55
Contractor's fee	(Direct cost+indirect cost)*0.05
Contingency	(Direct cost+indirect cost)*0.10
Startup and validation cost	(Direct fixed capital)*0.05

PC= Equipment Purchase Cost

DC= PC+ Installation+ A+B+C+D+E+F+G (4.1)

Indirect Cost= H+I (4.2)

4.1.2. Direct Cost

Equipment Purchase Cost: This cost represents the selling prices of equipments needed to run this facility and taxes, installation, insurance, delivery costs are not included in this cost.

Installation Cost: This cost represens the installation effort of new equipments on site and includes basis, auxiliary equipments, supports and plates needed for the installation.

Process Piping Cost: This item includes pipe supports, insulation, pipe connection, valves and ventilation systems connections.

Instrumentation: This item includes costs of the computers, data collecting, devices, control systems, measuring devices, and imaging devices inside the control room.

Insulation: This item includes the costs of insulation and painting spending for pipes. This cost depends on the facilities because some of the facilities require very hot, very cold, or ambient temperatures.

Electrical Cost: The cost of electricity is the cost of electrical equipment in the facility. This includes cabling and piping, control centers, transformer, lighting, emergency power supplies.

Buildings: The cost of building is the cost of walking ways, dressing rooms, canteens, towers, concrete, furniture in the offices, warehouse and security stuffs.

Yard Improvements: The cost of yard improvement is the cost of making field suitable for facility installation. Besides that, it includes the cost of road and park needed for the field.

Auxiliary Facilities: The cost of auxiliary facilities is the cost to make process run without any problems. This includes unpredictable tools needed to run facility.

Sum of the above 9 items represents total plant direct cost as given in the equation 4.1.

Table 4.3: Amount of equipments and and purchasing cost of a process which can operate 17 tons of biomass in one hour.

Equipment	Explanation	Quantity	Unit Price ($)	Total ($)
Decanter Centrifuge	Throughput = 4,86 m^3/h	2	230.000	460.000
Stirred Reactor	Vessel Volume = 42,02 m^3	1	859.000	859.000
Stirred Reactor	Vessel Volume = 22,03 m^3	1	718.000	718.000
Distillation column	Column Volume = 64,81 m^3	1	181.000	181.000
Stirred Reactor	Vessel Volume = 16,52 m^3	1	687.000	687.000
Fermentor	Vessel Volume = 758,11 m^3	1	3.650.000	3.650.000
Distillation Column	Column Volume = 9,96 m^3	1	60.000	60.000
Mixer	Rated Throughput = 43,00	1	40.000	40.000
Rotary Vacuum Filter	Filter Area = 33,13 m^2	1	126.000	126.000
Rotary Vacuum Filter	Filter Area = 51,40 m^2	2	150.000	300.000
Crystallizer	Vessel Volume = 151,83 m^3	1	1.446.000	1.446.000
Rotary Vacuum	Filter Area = 59,66 m^2	1	174.000	174.000
GAC Column	Column Volume = 27,58 m^3	15	294.000	4.410.000
Unlisted Equipment	-	-	-	3.278.000
			Total ($)	16.423.000

4.1.3. Total Plant Indirect Cost

This cost is the sum of the engineering and construction costs.

- Engineering: This cost of engineering is the cost of designings of equipments, tools, software, process control, technical specifications and drawings. For the economical evaluation, engineering cost is assumed to be 55% of direct cost.
- Construction: It represents the spendings regarding construction of the facility. However, it does not involve laboring for construction. For the economical evaluation, construction cost is assumed to be 55% of direct cost.

4.1.4. Contractor's Fee & Contingency

While calculating direct fixed capital cost, contingency and contractor’s fee are also considered and All of the above costs are listed in the (Table 4.4.)

- Contractor’s Fee: This cost represents to hire a construction company to build a new facility.
- Contingency: This cost represents unpredictable costs, and delays come up during the project. It has to be paid to run the project without any problems.

Table 4.4: Fixed capital cost estimation for a commercial scale of FDCA and bioethanol production.

A. Total Plant Direct Cost (TPDC) (physical cost in $)	
1. Equipment Purchase Cost	16.423.000
2. Installation	4.747.000
3. Process Piping	4.927.000
4. Instrumentation	4.869.000
5. Insulation	164.000
6. Electrical	1.642.000
7. Buildings	4.927.000
8. Yard Improvement	1.642.000
9. Auxiliary Facilities	3.285.000
TPDC	42.683.000
B. Total Plant Indirect Cost (TPIC)	
10. Engineering	10.671.000
11. Construction	14.939.000
TPIC	25.610.000
C. Total Plant Cost (TPC = TPDC+TPIC)	
TPC	68.292.000
D. Contractor's Fee & Contingency (CFC)	
12. Contractor's Fee	3.415.000
13. Contingency	6.829.000
CFC = 12+13	10.244.000
E. Direct Fixed Capital Cost (DFC = TPC+CFC)	
DFC	78.536.000

Utility cost is calculated by the unit price of electricity, steam and cooling water and the consumed amount and listed in (Table 4.5.) According to that, total annually utility cost is calculated 6.8 million $.

Table 4.5: Utility costs of the process to operate 17tons biomass/h.

Utility	Annual Cost ($)	%
Std Power	1.647.312	23,59
Steam	143.559	2,06
Steam (High P)	1.156.279	16,56
Cooling Water	903.578	12,94
Chilled Water	2.171.833	31,10
CaCl2 Brine	961.768	13,77
Total	6.984.329	100,00

4.1.5. FDCA and Bioethanol Production Process

Production of FDCA and bioethanol is designed by using Superpo Designer and flow diagram is given below (Figure 4.1.)

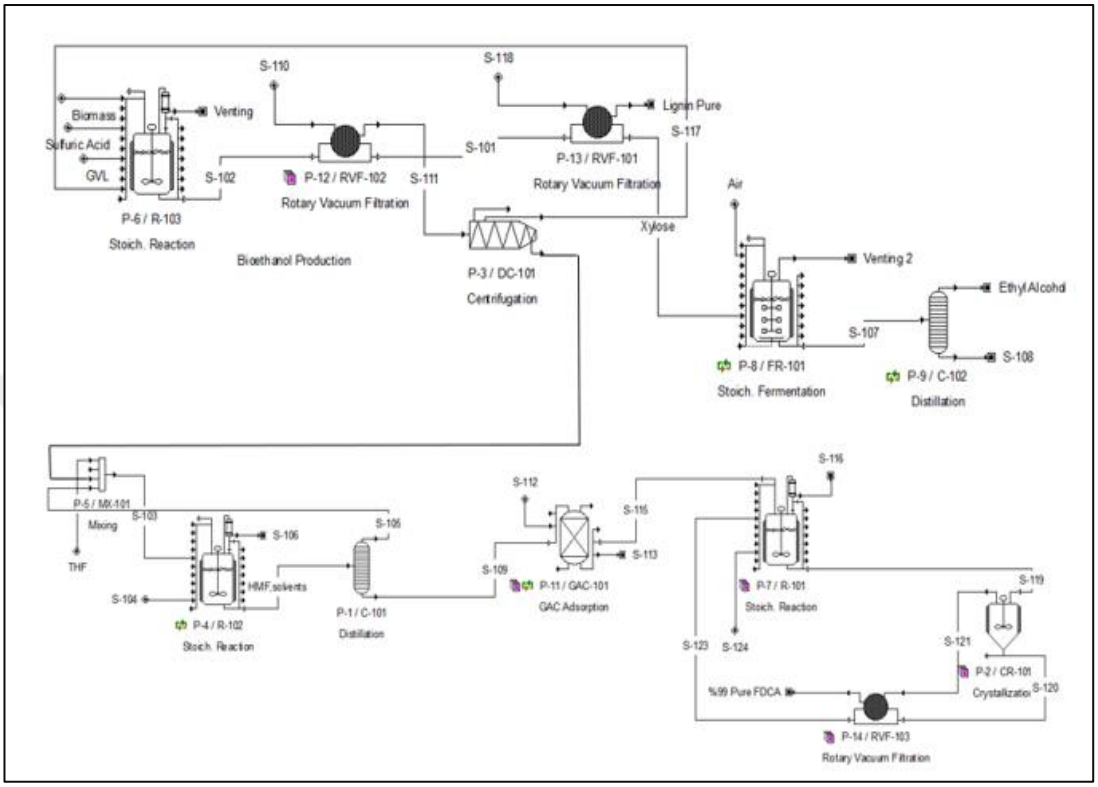


Figure 4.1: Flow diagram of FDCA and bioethanol production process.

The main revenues are obtained from FDCA, ethyl alcohol and lignin sales. Other potential revenue sources like wastes or gaseous are ignored. Net present value is calculated as below equation. CF represents cash flows, n represents the period number and i represents discount rate.

$$NPV = \frac{CF}{(1+i)n} - \text{Investment} \qquad (4.3)$$

Net present value is calculated153.174.000 $ at 2.0% interest rate, 86.947.000 $ at 5.0% interest rate, 36.560.000 at 10.0 % interest rate. In below 4.2 equation, PB represents payback period time and CF represents cash flow. For scenario 1, payback time is calculated as 5.23 years and for scenario 2, payback time is calculated as 2.49 years.

$$PB = \frac{Investment}{CF} \quad (4.4)$$

Table 4.6: Profitability Analysis.

A. Direct Fixed Capital	78.536.000 $
B. Working Capital	2.299.000 $
C. Startup Cost	3.927.000 $
D. Total Investment (A+B+C)	84.762.000 $
E. Revenue/Savings Rates	
Ethyl Alcohol (Revenue)	15.484.155 L/yr
Lignin Pure (Revenue)	16.996.455 kg/yr
%99 Pure FDCA (Main Revenue)	5.145.579 kg/yr
Steam (Savings)	945 MT/yr
Cooling Water (Savings)	13.716.469 MT/yr
F. Revenue/Savings Price	
Ethyl Alcohol (Revenue)	1,78 $/L
Lignin Pure (Revenue)	0,10 $/kg
%99 Pure FDCA (Main Revenue)	3,89 $/kg
Steam (Savings)	3,00 $/MT
Cooling Water (Savings)	0,05 $/MT
G. Revenues/Savings ($/yr)	
Ethyl Alcohol (Revenue)	27.561.796
Lignin Pure (Revenue)	1.699.646
%99 Pure FDCA (Main Revenue)	19.990.576
Steam (Savings)	2.835
Cooling Water (Savings)	685.823
1.Total Revenues	49.252.018
2. Total Savings	688.659
H. Annual Operating Cost (AOC)($/yr)	
1. Actual AOC	41.472.000
2. Net AOC (H1-G2)	40.783.000
J. Unit Production Cost /Revenue ($/ton MP)	
Unit Production Cost	7.311,66
Net Unit Production Cost	7.190,26
Unit Production Revenue	8.683,31
L. Gross Profit (G1-H2) ($/yr)	8.469.000
M. Taxes (35%) $/yr	2.964.000
N. Net Profit (L-M +Depreciation) $/yr	16.163.000
Gross Margin (%)	17,19
Return On Investment (%)	19,07
Payback Time (years)	5,24

4.1.6. Scenario 2

In this study, operated amount of biomass is increased from 17 tons/h biomass to 34 ton/h biomass to investigate the effect on purchased equipment costs and profitability. Process flow diagram, coefficient taken from SuperPro Designer, major economic parameters, assumptions, project life time, interest rate are taken same with the rate of 17 tons biomass/h. Equipment purchase cost is increased 55.8% compared to the process which can operate 17 tons of biomass in one hour and resulted $25.4 million. The biggest portion belongs to GAC column with 34.8%.

Table 4.7: Amount of equipments and and purchasing cost of a process which can operate 34 tons of biomass in one hour.

Equipment	Explanation	Quantity	Unit Price ($)	Total ($)
Decanter Centrifuge	Throughput = 6,48 m^3/h	3	230.000	690.000
Stirred Reactor	Vessel Volume = 10,24 m^3	1	636.000	636.000
Stirred Reactor	Vessel Volume = 22,02 m^3	1	718.000	1.436.000
Distillation column	Column Volume = 64,81 m^3	1	181.000	181.000
Stirred Reactor	Vessel Volume = 31,67 m^3	1	814.000	814.000
Fermentor	Vessel Volume = 1516,14 m^3	1	5.563.000	5.563.000
Distillation Column	Column Volume = 27,37 m^3	1	108.000	108.000
Mixer	Rated Throughput = 20,82 ton/h	1	40.000	40.000
Rotary Vacuum Filter	Filter Area = 66,25 m^2	1	175.000	175.000
Rotary Vacuum Filter	Filter Area = 68,53 m^2	3	178.000	534.000
Crystallizer	Vessel Volume =94,63 m^3	1	1.274.000	1.274.000
Rotary Vacuum Filter	Filter Area = 114,50 m^2	1	258.000	258.000
GAC Column	Column Volume = 27,58 m^3	30	295.000	8.850.000
Unlisted Equipment	-	-	-	5.140.000
			Total ($)	25.699.000

Total plant direct cost is calculated again as explained in (Table 4.2.) and listed in (Table 4.8.) Accordingly, total plant direct cost is calculated as 66.8 $ million, total plant cost is calculated as 106.9 $ million, contractor's fee and contingency is calculated as 16.0$ million, direct fixed capital cost is calculated as 122.9 $ million. In overall, direct fixed capital cost is increased 40.1% compated to 17 tons/h biomass.

Table 4.8: Fixed capital cost estimation for a rate of 34 tons/h biomass.

A. Total Plant Direct Cost (TPDC) (physical cost in $)	
1. Equipment Purchase Cost	25.699.000
2. Installation	7.448.000
3. Process Piping	7.710.000
4. Instrumentation	7.710.000
5. Insulation	257.000
6. Electrical	2.570.000
7. Buildings	7.710.000
8. Yard Improvement	2.570.000
9. Auxiliary Facilities	5.140.000
TPDC	66.812.000
B. Total Plant Indirect Cost (TPIC)	
10. Engineering	16.703.000
11. Construction	23.384.000
TPIC	40.087.000
C. Total Plant Cost (TPC = TPDC+TPIC)	
TPC	106.900.000
D. Contractor's Fee & Contingency (CFC)	
12. Contractor's Fee	5.345.000
13. Contingency	10.690.000
CFC = 12+13	16.035.000
E. Direct Fixed Capital Cost (DFC = TPC+CFC)	
DFC	122.935.000

Utilities of FDCA and bioethanol production facility consists of steam, electricity, cooling, heating etc. For this purpose, 10.0 million ton of chilled water, 19.3 million tons of cooling water, 1.298.938 million tons of $CaCI_2$ brine are comspumed. Total utility cost is calculated as 6.8 $ million which is 40% more than previous process.

Table 4.9: Utility costs of the process to operate 34 tons biomass/h.

Utility	Annual Cost ($)	%
Std Power	3.272.407	31,93
Steam	288.407	2,81
Steam (High P)	1.259.116	12,28
Cooling Water	1.053.047	10,27
Chilled Water	4.012.137	39,14
$CaCl_2$ Brine	365.094	3,56
Total	10.250.208	100,00

Total revenues are consists of lignin, FDCA and bioethanol. Accordingly, produced 31.1 million L/yr bioethanol, 33.9 million kg /yr lignin and 16.0 million kg /yr FDCA bring 121.2$ million revenue. In total, payback time is decreased to 2.48 and net profit is increased to 53.1$ million.

Table 4.9: Utility costs of the process to operate 34 tons biomass/h.

A. Direct Fixed Capital	122.935.000
B. Working Capital	3.697.000
C. Startup Cost	6.147.000
D. Total Investment (A+B+C)	132.778.000
E. Revenue/Savings Rates	
Ethyl Alcohol (Revenue)	31.117.621 L/yr
Lignin Pure (Revenue)	33.992.912 kg/yr
%99 Pure FDCA (Main Revenue)	16.079.931 kg/yr
Steam (Savings)	848 MT/yr
Cooling Water (Savings)	12.307.448 MT/yr
F. Revenue/Savings Price	
Ethyl Alcohol (Revenue)	1,78 $/L
Lignin Pure (Revenue)	0,10 $/kg
%99 Pure FDCA (Main Revenue)	3,89 $/kg
Steam (Savings)	3,00 $/MT
Cooling Water (Savings)	0,05 $/MT
G. Revenues/Savings ($/yr)	
Ethyl Alcohol (Revenue)	55.389.365
Lignin Pure (Revenue)	3.399.291
%99 Pure FDCA (Main Revenue)	62.470.530
Steam (Savings)	2.544
Cooling Water (Savings)	615.372
1.Total Revenues	121.259.188
2. Total Savings	617.916
H. Annual Operating Cost (AOC)($/yr)	
1. Actual AOC	65.920.000
2. Net AOC (H1-G2)	65.318.000
J. Unit Production Cost /Revenue ($/ton MP)	
Unit Production Cost	3.719,05
Net Unit Production Cost	3.685,03
Unit Production Revenue	6.841,10
L. Gross Profit (G1-H2) ($/yr)	55.942.000
M. Taxes (35%) $/yr	19.580.000
N. Net Profit (L-M +Depreciation) $/yr	53.046.000
Gross Margin (%)	46,13
Return On Investment (%)	39,95
Payback Time (years)	2,50

5. CONCLUSIONS AND RECOMMENDATIONS

This study aimed to make a techno-economical analysis of the production of FDCA from biomass via oxidation of HMF and bioethanol via fermentation of the xylose process. Facility feasibility analyses are made by using SuperPro Designer and evaluating different scenarios. To this end, the effect of parameters like raw material unit prices, interest rate, taxes percentages are investigated on the payback period time, profitability, and cash flow diagram. Lignin is separated from xylose and cellulose; in this process, lignin is also a revenue source. To summarize, FDCA, lignin, and bioethanol are main revenue sources. This study is roughly divided into below parts:

In the first part, pretreatment separates lignocellulosic biomass into components (cellulose, lignin, xylose, xylan). The reaction inlet temperature is 25°C, and the reaction pressure is 1.013 bar. As a heat transfer agent, chilled water was used at a rate of 447.02 ton/h, and heat transfer efficiency was 100.0 %. The residence time is 1 hour, and the working volume is 19.82 m^3. The reaction conversion rate is 95.0%.

In the second part, HMF is produced from cellulose. For that purpose, cellulose is purified using rotary vacuum filtration and centrifugation. The rotary vacuum filter has 0.0010 v/v cake porosity and 100 L/m^2*h average filtrate flux rate. This filter mainly separates cellulose and xylose into two different streams (S-111 and S-101, respectively). After that, cellulose is converted to HMF in a batch stoichiometric reactor at 221°C at 68 atm pressure with 37.91 m^3 working volume. Steam with high pressure is used as a heat transfer agent with 14.72 ton/h rates. The reactor has 4000 m^3 maximum volume, 6.974 m height, 2.779 m diameter, and the material of the reactor is selected SS316. The conversion rate of the reaction is 42%.

In the third part, FDCA is produced from HMF via catalytic oxidation in the continuous stoichiometric reactor. The reaction temperature is 110°C at 40 atm pressure with 15.68 m^3 working volume. Cooling water is used as a heat transfer agent. The reactor has 4000 m^3 maximum volume, 5.176 m height, 2.070 m diameter, and the material of the reactor is selected SS316. The reaction conversion rate is 93.6%.

The fourth part produces bioethanol from xylose via fermentation in batch operating mode. For that purpose, S-101 is fed to the rotary vacuum filter to separate xylose and lignin from each other. The filter had 0.0001 v/v cake porosity, 80 m^2 maximum filter area, and 33.18 m^2 filter area. The material of the filter is carbon steel. Lignin is completely separated from xylose. The xylose stream is fed to the

stoichiometric fermentor. The reaction temperature is 28°C at 1 atm pressure. The heat transfer agent is chilled water with 258 ton/h flow rate. The reactor has 682.3 m^3 working volume, 5.176m height, 2.070 m diameter, and the material of the reactor is selected SS316. After producing ethyl alcohol, it is distilled with a distillation column. The distillation column has 1atm pressure and 3.0 m/s vapor velocity. The condenser temperature is 79.6 °C, reboiler temperature is 80 °C. For condenser, cooling water is used as a cooling agent. For reboiler, steam is used as a heating agent. The minimum number of theoretical stages are 11.96, the number of theoretical stages are 23.5, stage efficiency is 80.0 %, number of actual stages are 30. Minimum reflux ratio is 5.5, R/Rmin is 1.25, reflux ratio is 6.9. Ethyl alcohol is selected as a light key, water is selected as a heavy key in the distillation column. Finally, ethyl alcohol is obtained with 97.4% purity.

In last part is FDCA purification via crystallization and rotary vacuum filtration. Crystallization operating pressure is 1 atm, the evaporating temperature is 210°C, the cooling temperature is 25 °C, and the working volume is 147.2 m^3. High pressurized steam is used as a heating agent, and chilled water is used as a cooling agent. The crystallization process is a continuous process. After crystallization, FDCA stream is fed to the rotary vacuum filter. The filter has 0.0011 v/v cake porosity, 500 m^2 maximum filter area, and 62.9 m^2 filter area. The material of the filter is carbon steel. Finally, FDCA is obtained with 99.9% purity as the main revenue.

Pretreatment technology and conditions of this method are critical for all biomass types and can affect the fermentable sugar concentration. However, there is a fact that no treatment technology converts biomass into fermentable sugars at 100% conversion rate. Follow-up two or three pretreatment technologies have shown higher efficiencies. In this study, GVL is chosen to separate biomass into its components because of its unique advantages such as low vapor pressure, renewable solvent, non-flammable, non-toxic, non-volatile, high solubility in lignin and sugar, and miscible with water. Furthermore, GVL treatment with a low amount of sulfuric acid addition is a suitable method for purifying lignin.

Lignin is separated from biomass with high purity (99.9%), and it is considered as a marketable product because of its wide application areas such as fuel(power), macromolecules, aromatics etc. As future work, lignin can be used inside the process to generate steam and reduce utility costs. Produced lignin can be fed to the steam-turbine generator and used to generate electricity. These steam and electricity can be

used inside the process to reduce the utility cost, which is calculated 6.8 $ million in scenario 1 and 10.0 $ million in scenario 2.

According to the results and other studies, increasing the facility capacity has a positive effect on facility feasibility and profitability. Doubling the biomass flow rate resulted in 52.4% decrease in return on investment period and increased the gross margin from 17.3% to 14.33%.

Modeling, optimization, and kinetic results found in this study may assist other studies or large-scale companies to lower their operational costs and change production methods. In this study, lignocellulosic biomass consisting of cellulose, lignin, water, xylan, and acetate is used. Components and percentages in the biomass are directly affecting the yield of FDCA and bioethanol. There are many pretreatment methods (physical, chemical, physicochemical, and biological) to be preferred for the process. The best pretreatment method is unclear, and the results may vary from biomass to biomass. Therefore, by choosing different biomass and pretreatment method, there can be many variants for the production of FDCA and bioethanol. In order to provide optimum efficiency, a plan should be created considering all variables.

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